



NRL/MR/6110--08-9169

# **Defining the Operational Conditions for High Temperature Polymer Fuel Cells in Naval Environments**

YANNICK GARSANY

OLGA BATURINA

KAREN SWIDER-LYONS

*Chemical Dynamics and Diagnostics Branch  
Chemistry Division*

December 31, 2008

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. <b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b>					
1. REPORT DATE (DD-MM-YYYY) 31-12-2008		2. REPORT TYPE Memorandum Report		3. DATES COVERED (From - To) 4th Quarter of FY-08 1 October 2008	
4. TITLE AND SUBTITLE  Defining the Operational Conditions for High Temperature Polymer Fuel Cells in Naval Environments				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)  Yannick Garsany, Olga Baturina, and Karen Swider-Lyons				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 61-9228-A85	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Naval Research Laboratory, Code 6113 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER  NRL/MR/6110--08-9169	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research ATTN Don Hoffman, Code 331 875 North Randolph St., Suite 1425 Arlington, VA 22203-1995				10. SPONSOR / MONITOR'S ACRONYM(S)  ONR	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT  A new high-temperature polymer fuel cell is emerging, based on phosphoric-acid-doped polybenzimidazole (PBI) membranes. PBI technology combines some of the benefits of both Proton Exchange Membrane Fuel Cells (PEMFCs) and phosphoric acid fuel cell technologies: a solid polymer electrolyte, the PBI membrane, but with higher temperature (160°C) operation. PBI membrane technology is far less developed than that for PEMFCs, but it is rapidly emerging as a possible candidate for naval fuel cell systems. With sponsorship from the Office of Naval Research, NRL evaluated the PBI membranes under varied poisoning conditions — sulfur impurity speciation: H <sub>2</sub> S and SO <sub>2</sub> ; impurity concentrations of 1 to 10 ppm — and examined strategies for contaminant cleanup and removal and fuel cell recovery. The finding of these studies is that PBI membrane electrode assemblies (MEAs) have approximately two orders of magnitude higher tolerance to sulfur contaminants in air than PEM MEAs. The performance of sulfur-poisoned PBI MEAs is completely recovered upon exposure to clear air.					
15. SUBJECT TERMS  Fuel cells					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  UL	18. NUMBER OF PAGES  14	19a. NAME OF RESPONSIBLE PERSON Karen Swider-Lyons
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (202) 404-3314



## Table of Contents

1. Overview .....	1
2. Results and discussion.....	2
A. Performance of PBI fuel cells .....	2
B. Effect of SO <sub>2</sub> air contaminants.....	4
C. Effect of H <sub>2</sub> S air contaminants.....	6
D. Comparison of polarization curves .....	7
3. Summary .....	8
Appendix: Experimental Procedures .....	10



# 1. Overview

NRL, with support from ONR, has been studying how air contaminants affect the properties of proton exchange membrane fuel cells (PEMFCs). PEMFCs operate at 80 °C, and are the present choice of fuel cell systems for the automotive market. Our research is showing how these fuel cells' platinum catalysts and membranes can be protected and recovered during and after exposure to the air impurities present in naval environments, including sulfur from munitions and salt air.

A new high-temperature polymer fuel cell is emerging, based on phosphoric-acid-doped polybenzimidazole (PBI) membranes. PBI technology combines some of the benefits of both PEMFC and phosphoric acid fuel cell technologies: a solid polymer electrolyte, the PBI membrane, but with higher temperature (160°C) operation. PBI membrane technology is far less developed than that for PEMFCs, but it is rapidly emerging as a possible candidate for naval fuel cell systems.

In the last quarter, we evaluated the PBI membranes under varied poisoning conditions, including:

1. Sulfur impurity speciation: H<sub>2</sub>S and SO<sub>2</sub>
2. Impurity concentration: 1 to 5 ppm
3. Strategies for contaminant clean up and removal, and fuel cell recovery.

The finding of these studies is that PBI MEAs have approximately two orders of magnitude higher tolerance to sulfur contaminants in air than PEM MEAs. The performance of sulfur-poisoned PBI MEAs is completely recovered upon exposure to clear air.

## 2. Results and discussion

### A. Performance of PBI fuel cells

The performance of a  $\text{H}_2/\text{Air}$  fuel cell with  $\text{H}_3\text{PO}_4/\text{PBI}$  membrane is shown in Figure 1 at constant current ( $0.2 \text{ A cm}^{-2}$ ) during the initial break-in procedure. The performance of the PBI fuel cell gradually increases in these 100 h. The voltage increases steadily in the first 60 h i.e. 0.66 V to 0.69 V, then a steady value of 0.70 V is obtained over the next 40 h.

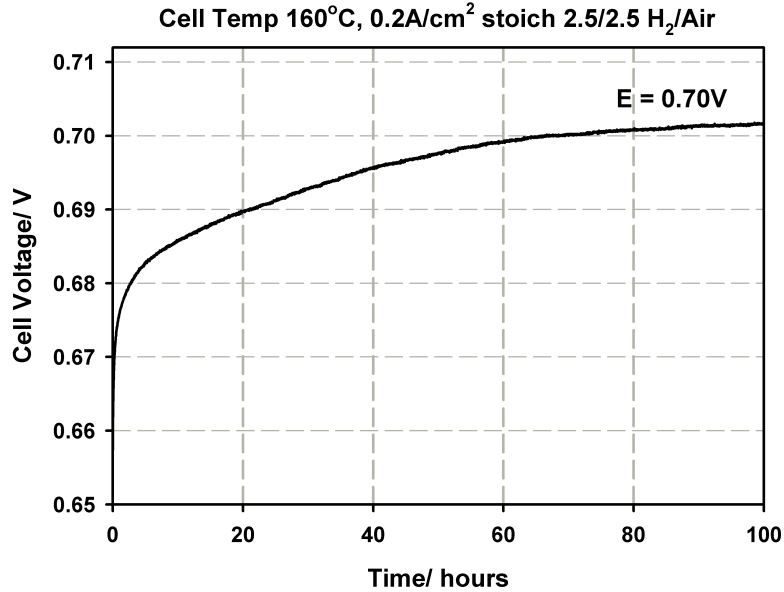


Figure 1: Steady state voltage plot of PBI MEA during activation phase under constant load ( $0.2 \text{ A cm}^{-2}$ ).

Figure 2 displays the  $iR$  corrected polarization curves obtained after the initial activation phase (break-in 100 h at constant current density of  $0.2 \text{ A cm}^{-2}$ ). The polarization curves show that the performance of the cell is constant and stable. The geometric cell resistance is also stable and low (i.e.  $0.076 \text{ Ohm cm}^{-2}$ ).

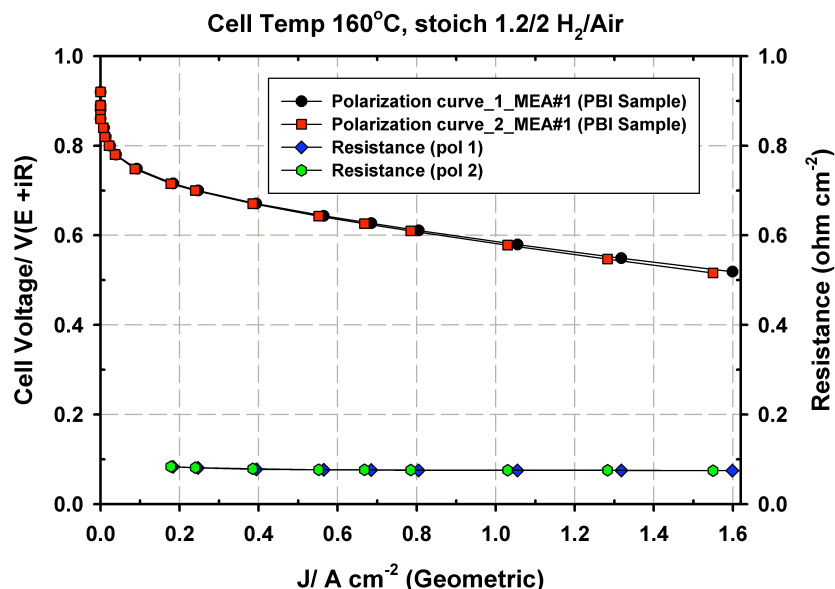


Figure 2: Polarization curves of PBI-based MEAs.

Figure 3 shows a CV for the cathode side of the MEA, a Pt alloy catalyst with a loading of  $0.77 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ . The electrochemical surface area (ECSA) was resolved from the hydrogen desorption area (see insert in Figure 3). Assuming that the charge came only from hydrogen interaction with the Pt surface, with a corresponding surface charge of  $210 \mu\text{C cm}^{-2}_{\text{Pt}}$ , an ECSA value of  $32 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$  was obtained.

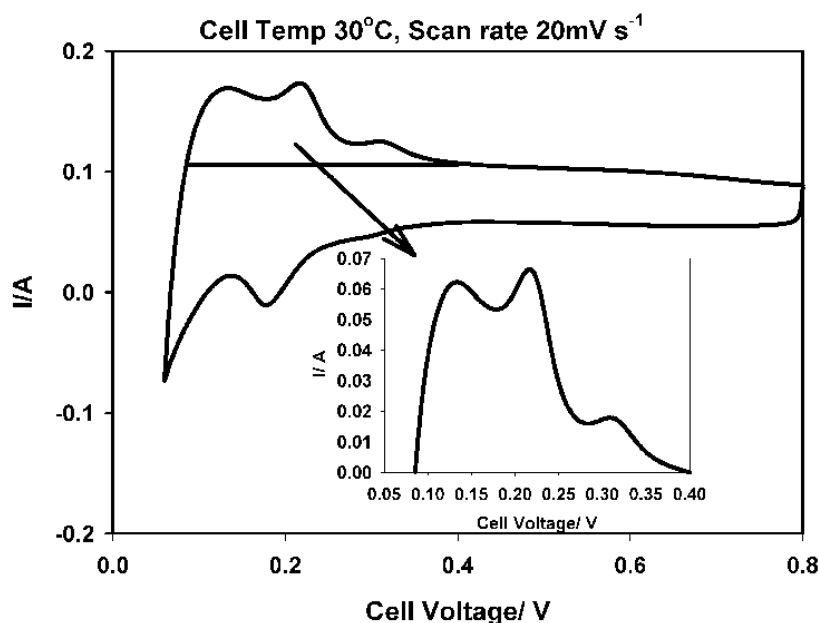


Figure 3: CV of a  $0.77 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  Pt alloy cathode of a PBI MEA at  $30^\circ\text{C}$  with dry  $\text{H}_2$  and Ar at ambient pressure using a sweep rate of  $20 \text{ mV s}^{-1}$ . The electrochemical surface area of the electrocatalyst was obtained from integration of the H desorption area (insert on Figure).



## B. Effect of SO<sub>2</sub> air contaminants

The performance of a PBI fuel cell with its cathode exposed to 1 ppm SO<sub>2</sub> for a total combine of 120 h is shown in Figure 4. The cell was first held at 0.68 V for 15 h under neat air to ensure that a constant current density was obtained. Little to no deterioration of the cell performance is observed within the first 24 h of poisoning for 1 ppm SO<sub>2</sub>. This result is very different from our findings with PEMFCs, which show that a fuel cell loses 83% performance upon exposure to 1 ppm SO<sub>2</sub>. In the PBI fuel cell, the current density,  $J$ , decreases  $4.5 \times 10^{-3} \text{ A cm}^{-2}$  (or 1.9%) in the first 24 h, and another  $2 \times 10^{-3} \text{ A cm}^{-2}$  (or 0.9%) after 96 h continuous exposure to 1 ppm SO<sub>2</sub>. The final value of  $J = 0.226 \text{ A cm}^{-2}$  is observed after 120 h continuous exposure to 1 ppm SO<sub>2</sub> (compare to  $J = 0.232 \text{ A cm}^{-2}$ , in neat air before SO<sub>2</sub> exposure). Overall, a 2.8% cell performance loss due to exposure to 1 ppm SO<sub>2</sub> for 120 h was observed.

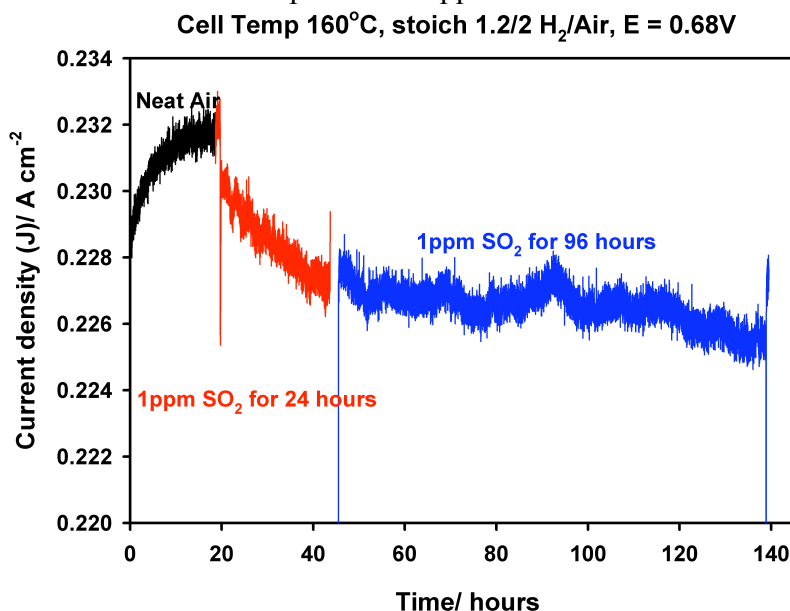


Figure 4: Transient response of a PBI MEA held at a cell voltage of 0.68 V while its cathode is exposed to air with 1 ppm SO<sub>2</sub>.

After 120 h continuous exposure to 1 ppm SO<sub>2</sub>, neat air was introduced to the cathode side for approximately 3.55 h. Then, the cathode side was exposed to 2.5 ppm SO<sub>2</sub> for 24 h. The transient response obtained for this exposure is shown in Figure 5. It can clearly be seen that the cell performance is almost totally recovered as the cathode side was purged with neat air for 3.55 h. A current density of 0.228 A cm<sup>2</sup> is observed after only 3.55 h, very close to the base line current density of 0.232 A cm<sup>2</sup> obtained after 15 h at 0.68 V prior to the 1 ppm SO<sub>2</sub> exposure (see Figure 4). Figure 5 also shows a steady but slow decrease in cell performance over the 24 h exposure to 2.5 ppm SO<sub>2</sub>. It should be noted that there is an initial drop of the current density (i.e. from 0.228 A cm<sup>-2</sup> to 0.224 A cm<sup>-2</sup>) as the SO<sub>2</sub> is introduced to the cathode side. This might be due to a temperature gradient between the 5 ppm SO<sub>2</sub> contaminant feeds and the incoming cathode air. The current density decreases from 0.224 A cm<sup>-2</sup> to 0.218 A cm<sup>-2</sup> after 24 h exposure to 2.5 ppm SO<sub>2</sub>. The cell performance is again totally recovered as neat air is introduced to the cathode side for about 2.5 h. A current density of 0.226 A cm<sup>-2</sup> is observed after 2.5 h exposure to neat air (compare to 0.228 A cm<sup>-2</sup> prior to 2.5 ppm SO<sub>2</sub> exposure).

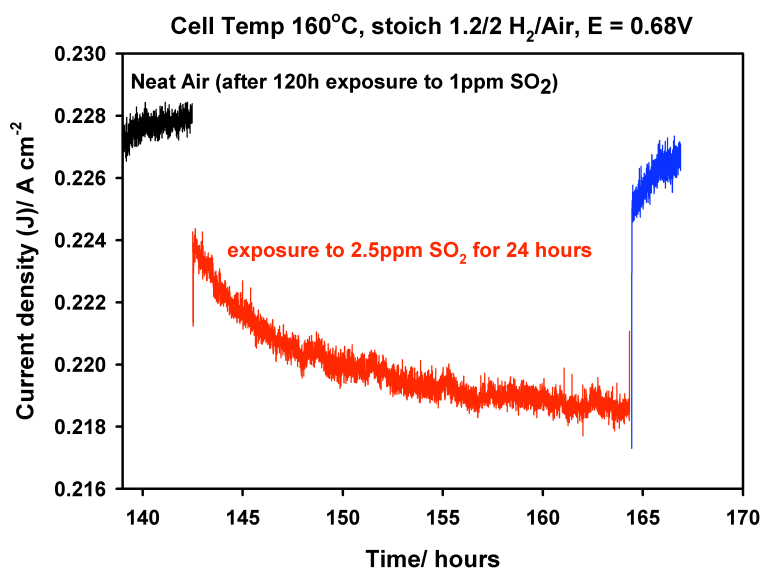


Figure 5: Transient response of a PBI MEA held at a cell voltage of 0.68 V while its cathode is exposed to air with 2.5 ppm SO<sub>2</sub>.

The same MEA is then subjected to exposure to 4.5 ppm SO<sub>2</sub> for 24 h. The current transient response obtained during this poisoning step is shown in Figure 6. Again, the trend seen with the lower SO<sub>2</sub> concentration is repeated. A slow but steady decrease of the cell performance is visible in the first 11 h, and then a constant current density of 0.210 A cm<sup>-2</sup> is reached. Again, total performance recovery was obtained when the cathode side was purged with neat air immediately after the 4.5 ppm SO<sub>2</sub> exposure (not shown).

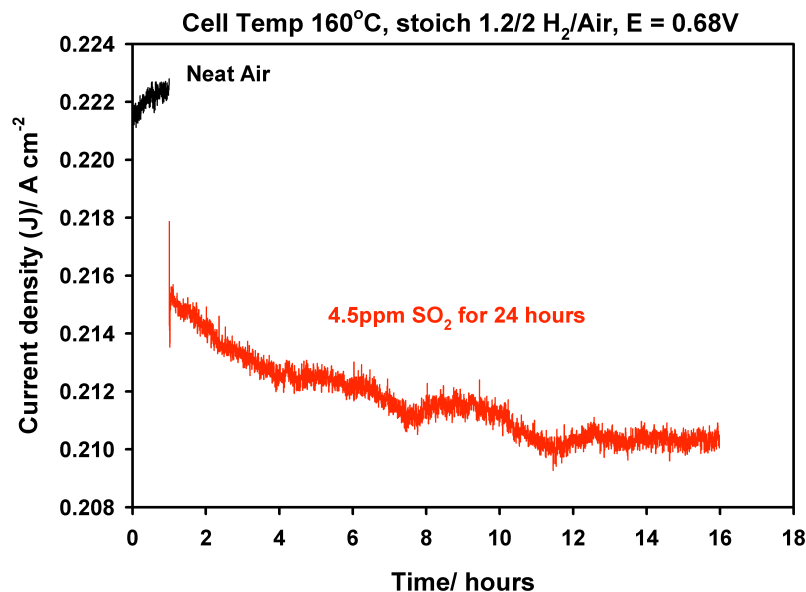


Figure 6: Transient response of a PBI MEA held at a cell voltage of 0.68 V while its cathode is exposed to air with 4.5 ppm SO<sub>2</sub>

### C. Effect of H<sub>2</sub>S air contaminants

Figure 7 reports the transient responses for the same MEA, but subjected this time to exposure to several different concentrations of H<sub>2</sub>S poisoning.

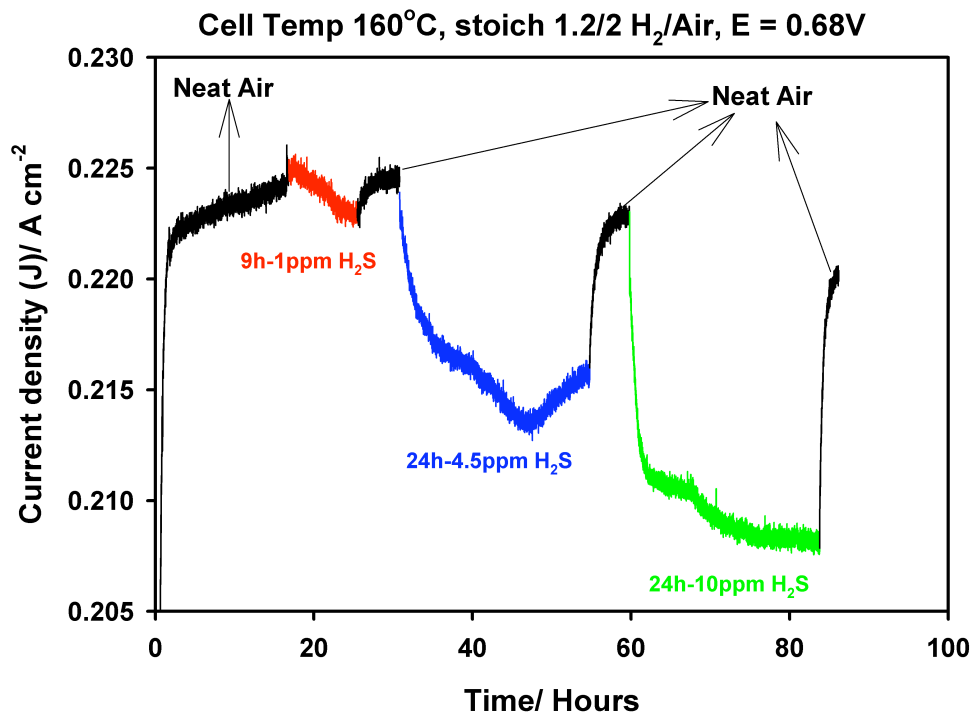


Figure 7: Transient response of a PBI MEA held at a cell voltage of 0.68 V while its cathode is exposed to air with 1, 4.5 , and 10 ppm H<sub>2</sub>S.

Figure 7 shows that 1 ppm H<sub>2</sub>S has very little effect on the performance of the cell. The current density decreases from 0.225 A cm<sup>-2</sup> to 0.223 A cm<sup>-2</sup> after 9 h exposure. Total performance recovery is achieved when the cell cathode is purged with neat air for 5 h directly after the poisoning step. During exposure to 4.5 ppm H<sub>2</sub>S for 24 h, the cell performance is slightly more effected. Again, as seen for SO<sub>2</sub> poisoning, there is a steady decrease in the current density, but a constant current density of 0.215 A cm<sup>-2</sup> is reached after 24 h exposure. This corresponds to a loss of only 4.4% of the initial current density. Purging the cathode side with neat air for 5 h led to almost total performance recovery. Increasing the concentration of H<sub>2</sub>S to 10 ppm led to slightly more pronounced performance loss. The current density decreases from 0.223 A cm<sup>-2</sup> to 0.208 A cm<sup>-2</sup> which corresponds to a 6.7% decrease in cell performance over 24h. Again, purging with neat air after exposure to 10 ppm H<sub>2</sub>S led to total cell performance recovery. It should be noted that the purging time between each poisoning step (i.e. 5 h) was set arbitrarily. It can be seen on Figure 7 that a steady state value has not yet been reached after 5 h. Therefore, it might be more appropriate to expand the purging time between each poisoning step to allow for full recovery.

#### D. Comparison of polarization curves

Figure 8 compares the iR corrected polarization curves for PBI MEAs obtained after the initial activation phase (break-in 100 h at constant current density of  $0.2 \text{ A cm}^{-2}$ ) and polarization curve obtained after all the poisoning experiments (i.e. after  $\text{SO}_2$  and  $\text{H}_2\text{S}$  poisoning experiments). Figure 8 clearly shows that the poisoning experiments had very little effect on the stability and overall performance of the PBI MEA.

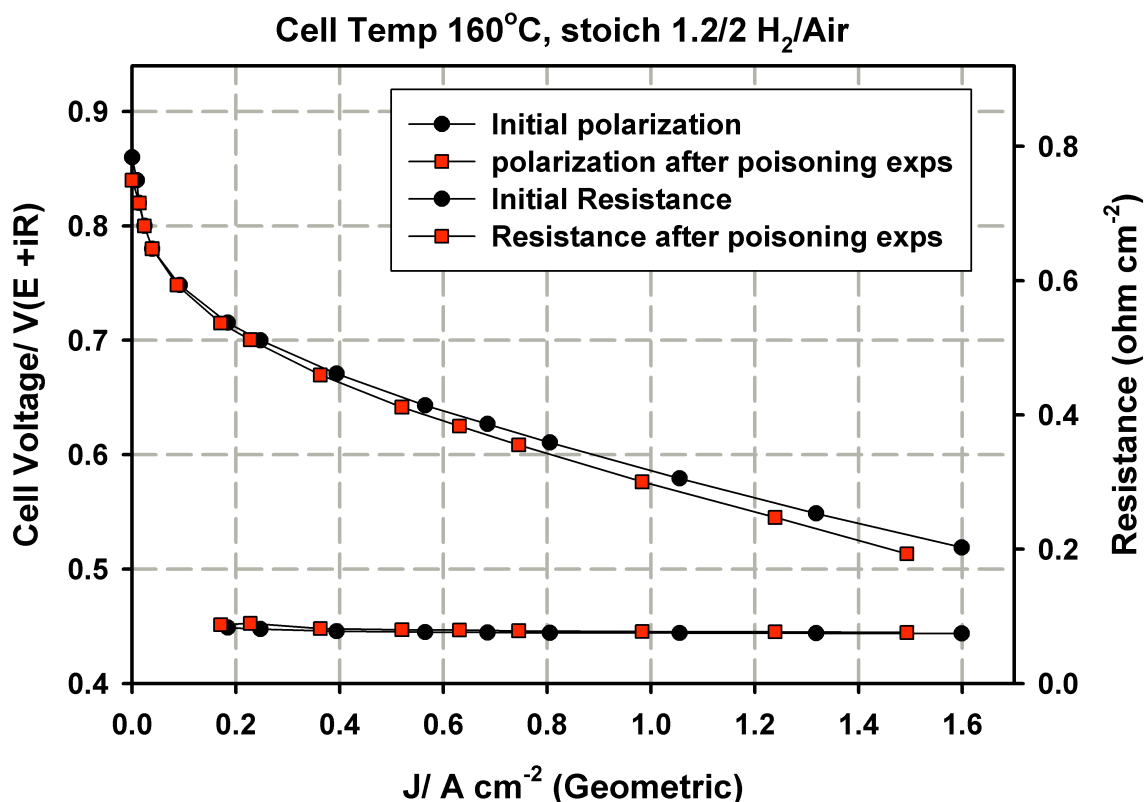


Figure 8: iR corrected polarization curves of PBI based MEAs, before and after poisoning.

### 3. Summary

PBI-based MEAs are hardly affected by contaminant exposures of up to 5 ppm of SO<sub>2</sub> and 10 ppm of H<sub>2</sub>S in air. Any poisoning is easily reversed by exposure to pure air.

The charts in Figures 9 and 10 summarize the performance of the PBI MEAs vs the results from our ONR-funded PEM studies, and the data are quantified in Tables I and II. The results show that the PBI is about 2 orders of magnitude more resistant to sulfur contaminants in air than the PEM MEAs. These results are consistent with the high poison tolerance observed at the anodes of PBI (M. Namazian, G. Venkataraman, S. Sethuraman, J. Strohm, C. Song, “Fuel Cell Power Generator (PJF-Gen),” SBIR Phase I Final Report, February 6, 2006, Contract Number N00014-05—M-0217, Office of Naval Research, ONR Program Manager: M. Anderson). The amount of SO<sub>2</sub> and H<sub>2</sub>S poisoning are also the same (within error), as observed in our PEM studies, suggesting that all gas-phase sulfur species equilibrate to a single sulfur species either during transport to or on the surface of the Pt electrocatalysts.

The likely reason for the poison tolerance of the PBI based MEAs is the weaker adsorption of S to the Pt-based electrocatalysts at their elevated temperatures (160 °C vs 80 °C for PEM MEAs). All of the results in this report must be repeated, and further experimentation is needed to explore the reasons for the high poison tolerance of the PBI MEAs.

Table I: Cell performance decrease (%) vs different time interval (h) for PBI and PEM MEAs exposed to 1 ppm SO<sub>2</sub>.

Exposure to 1ppm SO <sub>2</sub>	Time				
	1 h	3 h	9 h	12 h	24 h
PBI	0.81	1.0	1.3	1.6	1.9
PEM	19	52	78	82	83

Table II: Cell performance decrease (%) vs different time interval (h) for PBI and PEM MEAs exposed to 1 ppm H<sub>2</sub>S

Exposure to 1ppm H <sub>2</sub> S	Time				
	1 h	3 h	9 h	12 h	24 h
PBI	0.51	0.73	0.84	1.1	1.2
PEM	15	47	75	78	81

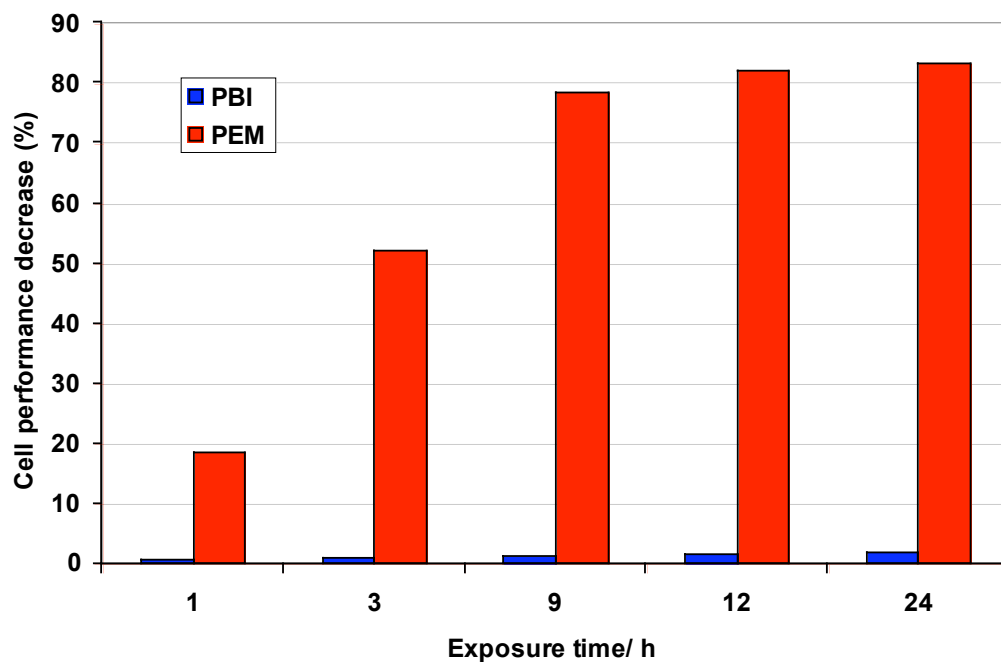


Figure 9. Cell performance decrease (%) vs different time interval (h) for PBI and PEM MEAs exposed to 1 ppm SO<sub>2</sub>.

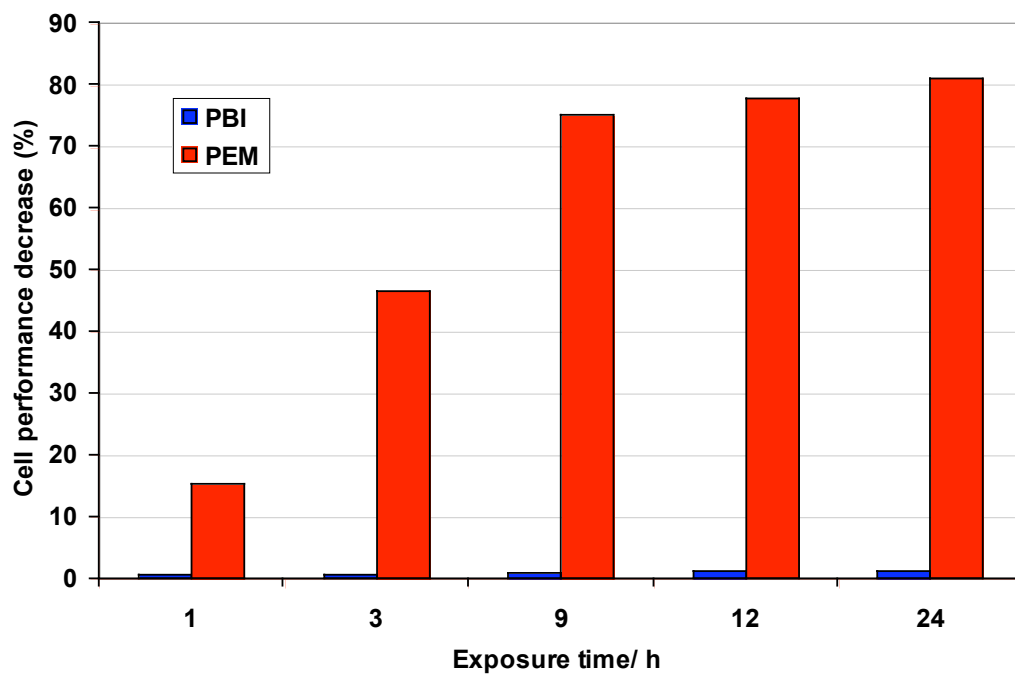


Figure 10: Cell performance decrease (%) vs different time interval (h) for PBI and PEM MEAs exposed to 1 ppm H<sub>2</sub>S

## Appendix: Experimental Procedures

### *Cell preparation and operating conditions:*

Commercially available membrane electrode assemblies (MEAs) from BASF were used in this study (Celtec-P series 1000). The catalyst-coated membranes (CCMs) consisted of two 10 cm<sup>2</sup> layers of catalyst inks deposited on opposite sides of a phosphoric acid doped polybenzimidazole membrane. The anode catalyst was Pt supported on Vulcan carbon with a Pt loading of 1.0 mg<sub>Pt</sub> cm<sup>-2</sup> and the cathode catalyst was a Pt-alloy supported on VC (presumably Pt-Ni/VC) with a Pt loading of 0.70 mg<sub>Pt</sub> cm<sup>-2</sup>.

A single cell was constructed by placing one MEA (the thickness of MEAs i.e. catalyst layers plus gas diffusion layers is 861 μm) between an anode side 320 μm gasket and cathode side 345 μm gasket inside a test fixture from Fuel Cell Technologies. Cartridge heated end plates, current collectors, Poco graphite flow fields with single serpentine flow channels, gaskets, GDLs, and the MEA were all sealed together with 8 bolts at 7 N·m of torque per bolt. Once assembled, the performance of the single cell MEA was tested using an 850e Fuel Cell Test System from Scribner Associates, Inc.

### *Start-up Conditions for Cell Testing:*

- The single cell was heated to 160°C with ultra high purity H<sub>2</sub> (99.999% Praxair) and ultra zero air (Praxair) gas flow as reactant gases with no additional humidification. No current was drawn to avoid condensation of water in the gases during heating from room temperature to operating temperature. The cell and gas pressure were kept at ambient pressure throughout the study.
- At 160°C, a current density of 0.2 A cm<sup>-2</sup> was set using stoichiometric gas flows (= 2.5 on both anode and cathode side).
- For optimum performance, the break-in was at least 100 hours.

After the conditioning period, polarization curves were taken at 160°C with an air/fuel stoichiometric ratio of 2/1.2 and the absolute flow dependent on the load. The polarization curves were comprised from measurements at the following voltages: 0.4, 0.45, 0.50, 0.55, 0.575, 0.60, 0.64, 0.68, 0.70, 0.74, 0.78, 0.80, 0.82 and 0.84 V. Each voltage was held for 15 minutes, though a steady state current was observed within the first few minutes. The current interrupt method was used to determine the cell resistance for correction to IR-free polarization curves.

The cell was then cool down to 30°C under a flow of 0.02 L min<sup>-1</sup> Ar to the cathode. Once the cell was cooled and the open circuit potential (OCP) had reached steady state, hydrogen adsorption/desorption data were collected via cyclic voltammetry (CV) for the purpose of determining the cathode catalyst's electrochemical surface area (ECSA). All CV measurements were performed using the anode under flowing H<sub>2</sub> as the reference electrode. CVs were performed from OCP to 0.80 V to OCP on the MEAs using an Autolab™ PSTAT30 potentiostat. The potential was swept at a rate of 50 and 20 mV s<sup>-1</sup> and plotted versus the corresponding current. The ECSA was determined from the charge consumed during hydrogen desorption between the OCP and 0.4 V, after double layer correction, assuming 210 μC cm<sup>-2</sup> as a conversion factor.

With characterization of the unpoisoned MEA complete, sulfur contamination experiments were commenced. The cell was heated back to 160°C and held at 0.68 V for 5 h until the current density was stable, with an air/fuel stoichiometric ratio of 2/1.2 and the absolute flow dependent

on the load. Once a baseline current density was established, sulfur species were introduced directly into the cathode air feed through a Teflon inlet downstream of the humidifiers. Certified mixtures of 5 ppm SO<sub>2</sub> in ultra zero air and 50 ppm H<sub>2</sub>S in ultra zero air (Praxair) were used as the starting compositions for the contamination studies. The 5 ppm SO<sub>2</sub> contaminant feeds was mixed with incoming cathode air and diluted down to 1, 2.5 and 4.5 ppm of sulfur species on a dry gas basis. Gas dilution was accomplished by two MKS mass flow controllers and the total gaseous flow rate into the cathode was maintained at 0.5 L min<sup>-1</sup> (dry). The cell was held at 0.68 V. The deactivation procedures with the different concentration of sulfur species were performed at an exposure time of 24 h. At the completion of the sulfur poisoning experiments, the cell was held at 0.68 V while the cathode was flushed with ultra zero air for 5 h to remove any traces of unreacted sulfur species in the experimental apparatus.



